The University of Chicago.
Founded by JOHN D ROCKEFELLER.

Studies in Catalysis.

IV. The Catalysis of Imidoesters.

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS OF ARTS, LITERATURE, AND SCIENCE IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

BY IRA H. DERBY.

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When an imidoester decomposes in an aqueous solution, at least[1] two reactions take place; in one the ester breaks down into a nitrile and an alcohol according to

$$RC(:NH)OR \rightarrow RCN + HOR \qquad (1),$$

and in the second one, minimal decomposition is affected through the agency of water, ammonia and an acid ester resulting according to

$$RC(:NH)OR + HOH \rightarrow RCOOR + NH_3 \qquad (2).$$

The velocity of the second reaction is enormously accelerated by the addition of an acid, much in the same way that the hydrolytic decomposition of an acid ester or cane sugar is accelerated in proportion to the concentration of the hydrogen ions of the acid added. According to Prof. Stieglitz[2] the latter, so-called catalytic, actions find their explanation simply in the formation of ionized salts of cane sugar and the esters with the added acid, in which the positive (oxonuim)

[1] An acid amide is very likely another by-product. The chief product is a nitrile. *Vide* Schlesinger's later paper.

[2] Report of the Congress of Arts and Science, St. Louis, Vol. IV., p. 276 (1904); Am. Chem. J., **39**, 29 and 402 (1908). *Vide* also Bredig: Z. Elek. Chem., **9**, 118 (1903).

ions of the organic compounds form the "active masses" which react with water; hence the action must obviously be accelerated in proportion to the increased concentration of these positive ions. These oxonium bases being so weak that exact measurements of the actual concentrations of their positive ions, under different conditions, by means of their affinity constants seemed for the time impracticable, the study of the parallel behavior of the closely related imidoesters was taken up, because all the necessary experimental data would be obtainable in this group.

At the suggestion and under the direction of Prof. Stieglitz I took up the problems of ascertaining experimentally what component in the solution of an imidoester gives rise to the decomposition expressed in (1), and especially of determining the active component in the more important reaction expressed in (2), on which the presence of an acid has a markedly accelerating effect. The second, more important reaction will be considered first.

The Action of Acids on Imidoesters.[1]

When an acid is added to an imidoester a condition of equilibrium is established between the weak base and its salt according to

$$RC(:NH_2Cl)OR' + H_2O \rightleftarrows RC(:NH_2OH)OR' + HCl \quad (3).$$

The reacting constituent in the decomposition accelerated by the addition of an acid can very readily be ascertained, then, by the determination, first, of the velocity of the decomposition, and, secondly, of the concentration of each component of the system at any moment t, and by the application of the laws of chemical equilibrium and dynamics to the data obtained. The work resolved itself, then, (1) into the development of simple, rapid methods of analysis for following the velocity of the deomposition of the imidoesters by water, (2) into the determination of the hydrolysis constants in the equilibrium equation of the hydrolyzed salt (equation 3), that is,

[1] For the theoretical and mathematical treatment of the problems reference is made to papers of Dr. Stieglitz, published in the Am. Chem. J. This paper is to deal only with the experimental work.

of the affinity constants of the imidoesters, from which the concentrations of the components of the system could be calculated, and (3) into the measurement of the velocities of decomposition of a number of imidoesters under various conditions.

The Methods of Analysis.

The simplest method of following the decomposition of a salt into ammonium chloride and an acid ester, according to

$$RC(:NH_2Cl)OR + HOH \rightarrow RCOOR + NH_4Cl \qquad (2'),$$

was suggested by the fact that the free imidoesters of the aromatic acids are oils or solids which are usually rather difficultly soluble in water but easily soluble in organic solvents like chloroform or carbon tetrachloride. The second basic ingredient in the mixture, ammonia, is, on the other hand, exceedingly soluble in water and extremely little soluble in the organic solvents. It was found, in fact, that after the addition of an alkali like sodium hydroxide the two bases could be separated quantitatively from dilute solutions by means of carbon tetrachloride, which was given the preference because of its greater density and cheapness as compared with chloroform.

Two simple methods of analysis were based on this separation. The shorter one, which was most frequently used, is as follows: If the bases are liberated from these salts in a measured portion of the mixture represented by the expression (2'), by the addition of a measured amount (v_1 cc.) of tenth-normal alkali, and the free imidoester is removed by carbon tetrachloride, the alkali is neutralized by the acid of the imidoester salt, exactly as if it were free hydrochloric acid; but with the ammonium chloride the alkali simply sets free the equivalent amount of ammonia which remains quantitatively in the aqueous solution. If, after the removal of the free ester by extraction with carbon tetrachloride, the aqueous liquid is titrated to neutrality by use of tenth-normal acid (v_2 cc.), in the presence of an indicator (methyl orange) sensitive to ammonia, the difference between the volume of the

standard alkali and acid used (v_1—v_2) represents the alkali neutralized by the acid of the ester salt. This quantity diminishes as the decomposition proceeds, ammonium chloride replacing the imido salt. In the actual work an aliquot portion (usually 25 cc.) of the solution under investigation was run into a measured excess (one and a half times the calculated amount) of tenth-normal alkali contained in a Squibb separatory funnel, the imidoester removed by three extractions with 20, 15, and 10, or 15, 10, and 5 cc. of carbon tetrachloride and the aqueous residue washed into an Erlenmeyer flask and neutralized in the presence of methyl orange. The accuracy of the method is shown by the results given in Table I., in which the weight of imidoester salt used for analysis is given in the first column, the weight of ammonium chloride mixed with the imidoester salt taken is given in the second column, and the actual volume of tenth-normal alkali used to neutralize the acid from the imidoester salt and the calculated amount required for the neutralization are listed in columns three and four, respectively. Ammonium chloride was added in the amount in which it was likely to be present in actual work in order to prove that within the limits of accuracy desired no ammonia is lost by the carbon tetrachloride extraction.

Table I.— Hydrochloride of Ethyl Imidobenzoate.[1]

Ester salt.	Ammonium chloride.	$v_1 - v_2$ used.	$v_1 - v_2$ calculated.
....	0.096	0.02	0.00
....	....	0.03	0.00
0.2313	....	12.28	12.45
....	0.070	0.22	0.00
....	0.070	0.14	0.00
0.1940	....	10.40	10.45
0.2046	....	11.05	11.07
0.2058	0.098	11.00	11.14
0.1252	0.039	6.74	6.74
0.0573	0.061	3.15	3.08
0.0409	....	2.16	2.20

The other and longer method of analysis is based on the same general principle as the one just given, but differs from it in

[1] Check analyses were made with all the imidoesters used but will not be reported. The method was always reliable for the aromatic esters.

that the imidoester base is determined directly. The imidoester was taken up from the combined carbon tetrachloride extract by shaking this with a measured excess (two or three times the calculated amount, in two successive portions) of tenth-normal sulphuric acid, and then the excess of acid neutralized by standard alkali in presence of an indicator (methyl orange or alizarinsulphonate) sensitive to the imidoester base. The carbon tetrachloride was washed with water after two extractions with the standard acid and the aqueous and acid extracts were mixed and titrated. As the imidoesters are much weaker bases than ammonia, methyl orange is not as sensitive to them as to ammonia, and the hydrochlorides of the esters react very slightly acid to methyl orange; so slightly that they produce in moderate dilutions, not strong acid tints (pink or red), but a brownish-pink color. A standard color of this tint was made for comparison and used for the end point in the titrations. For very accurate work standard tints were made for the various concentrations of salt used, since the degree of hydrolysis (equation 3) depends, of course, on the dilution. This last precaution was rarely necessary. While the method is longer and less convenient than the first one described, it was useful especially in determining the velocities of decomposition of the imidoester salts in the presence of added excess of the imidoester base. The degree of accuracy of the method is shown by the results given in Table II. The data in the various columns have the same significance as in Table I., except that in columns three and four the volumes are of tenth-normal acid instead of alkali.

Table II.—Hydrochloride of Ethyl Imidobenzoate.

Ester salt.	Ammonium chloride.	$v_1 - v_2$ used.	$v_1 - v_2$ calculated.
0.2313	....	12.27	12.45
....	0.070	0.10	0.00
....	0.070	0.12	0.00
0.1940	....	10.42	10.45
0.2046	....	11.02	11.07
0.2058	0.099	111.10	11.14
0.1252	0.039	6.78	6.74
0.0573	0.061	3.30	3.08
0.0409	....	2.30	2.20

PREPARATION OF THE IMIDOBENZOIC ESTER HYDROCHLORIDES AND IMIDOBENZOIC ESTERS.

The Imidoester Hydrochlorides.

Particularly pure imidoester salts being desired for these determinations, their preparation by Pinner's general method, with certain modifications, will be briefly described.

According to the method of Pinner[1] they were prepared by mixing equimolecular amounts of the carefully purified and dehydrated nitrile and alcohol and saturating the mixture, at o°, with dry hydrogen chloride. The reaction

$$RCN + ROH + HCl = RC(NH_2Cl)OR \qquad (4)$$

results after a few hours' standing. By this process a very hard, crystalline mass is obtained which it is difficult to break up and still harder to free from the excess of hydrochloric acid. If, however, three or four times their volume of dry ether is added to the mixed nitrile and alcohol and the whole is then saturated with hydrogen chloride, the resulting salt is loosely, finely crystalline, easily handled and purified. The yield is not diminished, for most of the imidoester salts are quite insoluble in ether. The product was purified by filtering off the crystals and washing them with dry ether, after which the salt was kept for some time under reduced pressure in a vacuum desiccator so that all ether and free hydrochloric acid might be removed. To obtain a perfectly pure product, further processes were resorted to in special cases and will be described in those connections. These salts are thus easily prepared in quantity but are difficult to keep, since traces of moisture produce decomposition, and by long standing even the dry salt very slowly undergoes spontaneous decomposition. Two of the products of decomposition were easily shown to be ammonium chloride and benzamide by the following methods: Ammonium chloride is nearly insoluble in absolute alcohol while the imidoester hydrochlorides are freely soluble. A sample of the imidoester salt, which had stood for some time, left a considerable amount of a white, crystalline residue after the imidoester had been

[1] Pinner: The Imidoesters.

dissolved out by absolute alcohol. A portion of this white residue, after drying, gave, on analysis, 66.06 per cent chlorine instead of 66.22 per cent, the theoretical amount for ammonium chloride. The alcoholic solution was evaporated *in vacuo*. An ether extract of the crystalline residue gave a substance which melted at 125°, while benzamide melts at 128°.

The Imidobenzoic Esters.

Imidobenzoic ester hydrochlorides, when treated with alkali hydroxide in cold solutions, yield immediately the imidobenzoic ester and an alkali chloride according to this general reaction:

$$RC(NH_2Cl)OR + MOH \rightarrow RC(NH)OR + MCl + H_2O.$$

These imidoesters are colorless, highly refracting oils, or white to pale yellow solids heavier than water and little soluble in that medium, but readily soluble in alcohol and ether. The general method of preparation finally adopted was as follows, preliminary experiments having shown that the preparation of pure esters is accompanied by many difficulties. Into a separatory funnel was placed sufficient of a 5–10 per cent sodium hydroxide solution for the complete decomposition of the imidoester salt, ether was added, and the whole cooled in ice water. The cooling minimizes the decomposition of the salts. To this cold solution the solid imidoester hydrochloride was added in successive small portions while the mixture was constantly agitated to facilitate the extraction of the liberated imidoester by the ether layer. The extract was then treated with fused calcium chloride in sticks and allowed to stand for an hour or more, usually in ice water. The mixture was shaken frequently to insure drying of all parts of the ether solution. Finally the ethereal solution was siphoned from the drying agent through a dry filter into a dry flask, when the drying process was again repeated and followed by one or two more repetitions. The success of the preparation and the purity of the final product depends very much on the thorough removal of the water from the ether solution. The ether was then driven off by distillation over a water bath and the residue, if an oil, was fractionally distilled *in vacuo*;

if a solid, it was purified by recrystallization. All the esters, on standing, even in sealed tubes, decompose to a greater or less extent, and long, colorless, highly refracting, prismatic crystals separate from the liquids. In all the work where pure substances were necessary, freshly prepared esters or recently distilled portions were always used. The imido-esters were always analyzed by titrating a weighed amount, mixed with 25–30 cc. water, directly with tenth-normal acid (usually sulphuric acid) in the presence of methyl orange, that tint of red being used as the end point which was most nearly like the tint produced by a corresponding weight of the pure imido hydrochloride when dissolved in the same volume of water with the addition of an equal amount of methyl orange.

Ethyl Imidobenzoate.

Ethyl imidobenzoate was made and analyzed as described above. The following table shows the boiling points of several preparations, with the accompanying analyses. Column one shows the boiling point; two, the corresponding pressure; three, the weight of the ester taken for analysis; four, the amount of tenth-normal acid used; and column five, the calculated volume of tenth-normal acid required for the same weight of pure substance.

Boiling point.	Pressure in millimeters.	Weight of esters.	Acid used.	Acid calculated.
115°.5	....	0.2902	19.42	19.46
115°	21.5	0.4319	28.92	28.96
115°	21.5	0.4048	27.14	27.14
101°–102°	11.0	0.2402	16.13	16.10

The boiling point at 744.7 mm. pressure was 219°. The boiling in this case was accompanied by slow decomposition, as was shown by analysis of the sample.

The pure product was a colorless, somewhat viscous liquid more dense than water and having an index of refraction of 1.5278 at 20°; it is miscible in all proportions with alcohol and ether, but only very slightly soluble in water. At 25° 100 cc. of aqueous solution was found to contain 0.396 gram of ethyl imidobenzoate, or a liter will dissolve 0.026 molecule.

The ester is soluble in carbon tetrachloride and three determinations were made to find out its partition coefficient between water and carbon tetrachloride, with the following results: C_1 and C_2 indicate the amounts of imidoester dissolved in 100 cc. of each solvent, respectively, while $K = C_2/C_1$ shows the partition coefficient. The temperature was 23° (+1°).

C_1.	C_2.	C_2/C_1.
0.0194	2.450	126
0.0114	1.464	128
0.0073	0.901	123

Methyl Imidobenzoate.

This substance, prepared by the method described, was obtained pure with much greater difficulty than was experienced with any of the other esters studied, and when it was obtained pure it soon changed, so that frequent fractional distillations were necessary to prepare and keep sufficiently pure material for the work.

The following table is in every respect similar to the one given in connection with the ethyl ester. It shows the results obtained with the methyl ester.

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
104°	20.5	0.4000	29.46	29.60
83°	5.8	0.3554	15.67	15.64
106°	22.0	0.2724	20.05	20.15
107°	22.5	0.2680	19.80	19.83
91°.8	11.0	0.2528	18.72	18.69
....	....	0.2097	15.43	15.40
101°	18.0	0.4862	35.81	35.98
98°	14.5	0.4227	31.27	31.28
99°.7	16.5	0.4202	31.07	31.09
75°.5	3.8	0.3171	23.51	23.47

The properties of the methyl ester differ from those of the ethyl ester only in degree. It is slightly more soluble in water. The index of refraction at 20° is 1.5430. At 10.5 mm. pressure the boiling point is 10° lower than that of the ethyl ester at the same pressure.

Normalpropyl Imidobenzoate.

This ester was prepared by the general method and analyzed in the usual way. It was obtained pure more readily than any of the other esters studied. The tendency to form benzamide was much less pronounced, as indicated by the very slight amount of solid residue remaining in the flask after the distillation *in vacuo*.

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
121°	16	0.1836	11.25	11.25
121°.1	16	0.2757	16.97	16.90
121°	16	0.2718	16.74	16.66

The normalpropyl ester appeared to be less soluble in water than its two homologues just described, but resembled them closely in properties. The index of refraction, as determined at 20°, was 1.5173.

Isopropyl Imidobenzoate.

The isopropyl ester was prepared like the other esters. It was obtained pure with much more difficulty than its isomer and, like the methyl ester, seemed to decompose somewhat into benzamide, a residue of which was usually obtained after the fractional distillation of the ester *in vacuo*. The boiling points under the reduced pressures, together with the analytical results, are given in the table:

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
102°	10	0.2106	12.80	12.90
106°	13	0.2239	13.66	13.72
....	..	0.2110	12.93	12.95
114°	20	0.2127	13.05	13.04
114°	19	0.2139	13.13	13.11

The properties were the same as for the isomeric normalpropyl ester. A rough determination of solubility at room temperature (about 21°) showed that 100 cc. of solution contained 0.161 gram of the ester. The index of refraction, at 20°, was 1.5144.

Methyl Metanitroimidobenzoate.

The free ester was prepared from the hydrochloride salt by the general method. It forms a solid.

This solid was pale yellow in color and very slightly soluble in water. It melted sharply at 50°.6 and was used for the experimental work to be described later. As is shown by its conductivity in aqueous solution at 25°, it contained nothing of such a nature as would vitiate the results. This conductivity was 4×10^{-6}.

THE AFFINITY CONSTANTS OF IMIDOESTERS BY THE CONDUCTIVITY METHOD.

The apparatus used for the work was of the kind ordinarily used in conductivity measurements; namely, a meter-wire bridge and resistance box, both of which were carefully calibrated, a specially wound induction coil, and a sensitive telephone. In some of the later work a short bridge was used. The scale on this was laid out in proportional parts. This was found sufficiently accurate for the work and much more convenient than the meter bridge. For maintaining a condition of constant temperature a large, rectangular, galvanized water bath, of about one cubic meter capacity and jacketed with asbestos, was fitted with a very large (about one liter) gas thermoregulator of the Ostwald type, filled with toluene. The water was kept thoroughly stirred by means of a four-armed, windmill-shaped stirrer run by an electric motor. After once being adjusted to 25°, this bath remained at a uniform temperature day and night for weeks, varying much less than 0°.01, as was shown by a series of observations made with a Beckmann thermometer. The level of the water in the bath was maintained constant by occasional additions so that the hydrostatic pressure exerted upon the regulator might be uniform. For the conductivity work at 18° a bath fitted up similarly to the one just described was used, except that in this case a cold water coil was essential to keep the water sufficiently cooled to enable the regulator to work.

Since the imidoester salts, when brought into water solution,

instantly begin to decompose, the ordinary method for obtaining the various concentrations, by means of successive dilutions of a concentrated solution of the substance, could not be used. Each solution investigated was made up separately by weighing the amount of salt required for 50–100 cc. of solution. This weighed amount of substance was then transferred to the dry Arrhenius cell, which had already been in the bath long enough to acquire the proper temperature, and the water for the solution, which was also at the bath temperature, was poured in. The salts are rapidly soluble, and when the electrodes were put in after the addition of the water and raised and lowered five or six times a homogeneous solution was obtained. During the time (never less than two minutes) required for the preparation of the solution, some change inevitably takes place and the first bridge reading corresponds, then, to the mixed solution of imidoester and ammonium chloride formed by the decomposition and not to the pure solution of imidoester hydrochloride, which could only be observed at zero time, a practical impossibility in this case. For getting this reading corresponding to zero time, a process of extrapolation was used. An inspection of a large number of series of measurements showed that during the first twenty or twenty-five minutes the changes in conductivity, consequently the change in bridge reading, was proportional, within the limits of experimental errors, to the time. For any given experiment, then, the exact time at which the water was poured in was noted, at the end of five minutes the first bridge reading was taken, followed by three or four more readings also at five minute intervals. From these bridge readings a simple numerical extrapolation gave the desired reading at zero time. An actual series of observations are here given to clearly illustrate this very important detail of the method. The columns in the following table have this significance: One shows the time in minutes; two, the bridge readings taken at the times given; three, the changes in bridge readings for each interval of five minutes and also the average; four, the total changes in bridge reading corresponding to each total time as calculated by means of the average difference

found from column three; and column five gives the zero-time readings of the bridge as calculated from each observed reading by adding the calculated corresponding total variations given in column four.

Time.	Bridge. Required.	Bridge difference.	Calculated total variations.	Bridge reading at zero time.
0	.....	..	..	.....
5	0.449	..	4	0.453
10	0.445	4	8	0.453
15	0.440	5	12	0.452
20	0.437	3	16	0.453
25	0.434	3	20	0.454
	Average,	4	Aver. for zero time,	0.453

The bridge reading corresponding to zero time, was, then, 0.453, and was used, together with the resistance and constant of the cell, to derive the specific conductivity of the solution at the instant of preparation. Another method by which the conductivity at zero time was obtained consisted in calculating each specific conductivity corresponding to each bridge reading and using these values in place of the bridge readings for the extrapolation calculation. This involves more calculations than the first method and, since the resulting values are nearly the same, the former method was most used.

THE HYDROLYSIS CONSTANTS FOR THE IMIDOESTER HYDROCHLORIDES.

Ethyl Imidobenzoate.

The data for the hydrolysis constant for the hydrochloride of ethyl imidobenzoate (equation 3) were determined, as described above, by Bredig's method.[1] The molecular conductivities, μ_v, for the nonhydrolyzed salt were first determined, the hydrolysis being suppressed by the addition of an excess of 0.025 and 0.0125 mole of free base. Two series of determinations were made and the results of these are summarized in Table III. Column one gives the volume in liters containing a gram molecular weight of the salt; columns two and three, the molecular conductivities, μ_v, in reciprocal

[1] Z. physik. Chem., **13**, 288 (1894).

mercury units, in the presence of 0.025 and 0.0125 mole, respectively, of free base; and columns four and five, the conductivity, μ_∞, of the nonhydrolyzed salt for infinite dilution, as calculated from the previous columns by the addition of the characteristic constants, Δ_v, of Ostwald and Bredig.[1]

Table III.

	0.25 base.	0.0125 base.	0.025 base.	0.0125 base.
V.	μ_v.	μ_v.	μ_∞.	μ_∞.
32	83.4	83.2	97.4	97.2
64	86.5	87.5	97.5	98.5
128	90.3	89.5	98.3	97.5
256	92.7	92.4	98.7	98.4
		Mean,	97.97	97.90
32	83.5	83.4	97.5	97.4
64	86.1	86.9	97.1	97.9
128	89.2	89.7	97.2	97.7
256	91.7	92.7	97.7	98.7
		Mean,	97.37	97.9

The agreement in the values for μ_∞ being satisfactory, both as regards the values obtained in the presence of varying amounts of free base and as regards the duplicate series, the following mean values were considered to represent the true molecular conductivities of the nonhydrolyzed salt at 25° (±0°.01):

V	32	64	128	256
μ_v	83.4	86.7	89.6	92.4

The conductivity of the hydrochloride was next determined in the hydrolyzed solution, without the addition of any free base, and the degree of hydrolysis calculated according to

$$x = \frac{M_{obs} - \mu_v}{\mu_{HCl(v)} - \mu_v},$$

in which M_{obs}, μ_v and $\mu_{HCl(v)}$ represent the molecular conductivities of the hydrolyzed salt, the salt, and hydrochloric

[1] *Loc. cit.* In later determinations (*vide* a later paper by E. E. Barnard) a more exact graphic method was used to obtain μ_∞.

acid, respectively, all referred to the same volume, the volume containing a molecular equivalent of total electrolyte.[1] The values which were used for the molecular conductivity of hydrochloric acid at 25° were those determined by Ostwald:

V	32	64	128	256	512
μ_{HCl}	369	374	376	378	379

Table IV. summarizes the results. Column one gives the volume, in liters, containing a gram molecule of the salt; two shows the observed molecular conductivity for the hydrolyzed salt; three, the degree of hydrolysis; and column four, the hydrolysis constant calculated from

$$\frac{(1-x)V}{x^2} = \frac{k_{base}}{k_{H_2O}} = K_{hydrolysis.}$$

Table IV.

V.	$M_{obs.}$	$100x$.	$10^{-5} \times K_{hydrolysis.}$
32	85.1	0.59	9.1
32	85.1	0.58	9.5
64	89.7	1.04	5.8
64	89.4	0.94	7.2
128	93.1	1.20	8.8
256	96.3	1.36	13.0
			Mean, 8.9×10^5

The affinity constant for ethyl imidobenzoate is then:

$$K_{aff.} = K_{hydrolysis} \times K_{H_2O} = 8.9 \times 10^5 \times 1.2 \times 10^{-14} = 1.1 \times 10^{-8}.$$

Methyl Imidobenzoate.

The experimental results for the determination of the constant for the hydrochloride of methyl imidobenzoate are given in Tables V. and VI. Table V. gives the data for the determination of the molecular conductivity of the nonhydrolyzed salt at various dilutions and the columns have the same significance as in Table III.

[1] Stieglitz and Derby: Am. Chem. J., **31**, 449 (1904).

Table V.

	0.25 base.	0.0125 base.	0.025 base.	0.0125 base.
V.	μ_v.	μ_v.	μ_∞	μ_∞
32	....	85.3	....	99.3
64	89.3	89.9	100.3	100.9
128	91.5	92.1	99.5	100.1
256	....	95.0	....	101.0
		Mean,	99.9	100.7
32	....	86.7	....	100.7
64	89.9	90.7	100.9	101.7
128	92.7	92.9	100.7	100.9
256	....	94.3	....	100.3
		Mean,	100.8	100.8

The mean of all of the values for the conductivity at infinite dilution was 100.5. The following values were taken as representing the molecular conductivities of the nonhydrolyzed salt:

V	32	64	128	256	512
μ_v	86.5	89.5	92.5	94.5	96.5

Following are the graphically interpolated values for intermediate dilutions corresponding to the four odd dilutions listed in Table VI.:

V	29.4	58.8	117.6	235.2
μ_v	86.1	89.0	91.8	94.2

Table VI. gives the observed conductivities of the hydrolyzed salt. The columns have the same significance as in Table IV.

Table VI.

V.	$M_{obs.}$	$100\,x$.	$10^{-5} \times K_{hydrolysis.}$
32.0	89.7	1.13	2.47
32.0	89.7	1.13	2.47
32.0	89.5	1.05	2.87
64.0	93.6	1.44	3.04
64.0	93.8	1.47	2.91
64.0	93.6	1.44	3.04
58.8	92.3	1.16	4.32
128.0	97.8	1.87	3.59
128.0	96.6	1.80	3.88
128.0	97.8	1.87	3.59
128.0	97.5	1.76	4.06

Table VI—(Continued).

v.	$M_{obs.}$	$100x$.	$10^{-5} \times K_{hydrolysis.}$
117.6	97.4	1.97	2.97
256.0	101.0	2.29	4.77
256.0	99.9	1.90	6.94
256.0	100.9	2.25	4.94
235.2	100.8	2.33	4.23
512.0	104.2	2.70	6.83

Mean, 3.93×10^5

The affinity constant for methyl imidobenzoate, as calculated from the hydrolysis constant, is 4.7×10^{-9}.

n-Propyl Imidobenzoate.

The following tables give the data for determining the hydrolysis constant of the *n*-propyl imidobenzoate. The significance of the columns is the same as in Tables III. and V The amount of free base present was sufficient to suppress the hydrolysis but was not accurately weighed out in each case, as was done in the determinations on the ethyl and methyl esters. The values for μ_∞ were obtained by graphic interpolation.

Table VII.

v.	μ_v.	μ_∞.	v.	μ_v.	μ_∞.
32	82.4	96.4	128	88.1	96.1
48	84.0	96.2	192	89.1	95.9
64	85.4	96.4	256	91.1	97.1
96	87.3	96.5	384	91.6	96.0

Mean, 96.3

Table VIII. gives the degree of hydrolysis and the value of the constant. The columns have the same significance as in Tables IV. and VI.

Table VIII.

v.	$M_{obs.}$	$100x$.	$10^{-5} \times K_{hydrolysis.}$
32	83.6	0.42	18.1
48	86.0	0.69	10.0
64	88.0	0.90	7.8
96	89.6	0.80	14.9
128	91.5	1.18	9.1
192	92.3	1.11	7.4
256	94.9	1.32	14.5

Mean, 12.8×10^5

The affinity constant, as calculated from the hydrolysis constant, is 15.4×10^{-9}.

Isopropyl Imidobenzoate.

Tables IX. and X. give the results of the conductivity measurements for isopropyl imidobenzoate, the degree of hydrolysis, and the value of the hydrolysis constant:

Table IX.

$V.$	$\mu_v.$	$\mu_\infty.$	$V.$	$\mu_v.$	$\mu_\infty.$
32	82.0	96.0	256	90.1	96.1
64	85.4	96.4	512	91.7	95.7
128	88.1	96.1	407.3	91.5	96.2

Mean, 96.08

Table X.

$V.$	$M_{obs.}$	$100\,x.$	$10^{-5} \times K_{hydrolysis.}$
32	83.6	0.56	10
32	84.2	0.76	6
64	87.3	0.65	16
128	90.6	0.86	17
256	93.0	1.00	25
256	93.8	1.28	15
512	96.5	1.66	18
407.3	96.2	1.63	15

Mean, 15×10^5

The value of the affinity constant, as calculated from the hydrolysis constant, is 1.8×10^{-8}.

Methyl Metanitroimidobenzoate.

Because of the great rapidity of decomposition of this body, the conductivity determinations were carried out at a temperature of 18°. The free methyl metanitroimidobenzoate base was found to be much less soluble than any of those previously studied and, for the determination of the conductivities of the nonhydrolyzed salt, a sufficient quantity of base was added to each solution so that a little remained undissolved after the thorough mixing preceding the measurements. To be absolutely sure that all hydrolysis was suppressed, each solution was tested with methyl orange at the end of the observations and proven to be a little alkaline in reaction.

Table XI.

$V.$	$\mu_v.$	$\Delta^1.$	$\mu_\infty.$
32	73.8	12.1	85.9
32	73.8	12.1	85.9
48	75.6	10.4	86.0
64	76.4	9.6	86.0
96	78.0	7.8	85.8
128	78.8	7.0	85.8
192	80.4	5.8	86.2
256	80.5	5.2	85.7
256	81.1	5.2	86.3
		Mean,	85.96

Table XII.

$V.$	$M_{obs.}$	$100\,x.$	$10^{-4} \times K_{hydrolysis.}$
32	79.25	2.10	7.1
48	82.83	2.77	6.1
64	84.85	3.20	6.1
96	88.84	4.12	5.4
128	91.70	4.91	5.1
192	94.73	5.45	6.1
256	99.30	7.16	4.6
		Mean,	5.8×10^4

The affinity constant[2] is then 3.7×10^{-10}.

The Affinity Constant of Ethyl Imidobenzoate Determined by a Colorimetric Method.

The determination consisted in simply taking equal volumes of water solutions of the hydrochloride of known concentration, placing them in color-comparison tubes with the same amounts of methyl orange, and adding standard acid to the water until the red tint matched the red of the salt solution employed. Knowing the volume of the water and the amount of standard acid used and the concentration of the imidoester hydrochloride, a simple calculation gave the amount of free acid formed by hydrolysis and the degree of hydrolysis. The following table, XIII., gives the results. Column one

[1] Bredig's differences refer to 25° C. A temperature correction of 0.019 per degree was used.

[2] KH_2O was taken as 0.64×10^{-14} at 18°, according to Arrhenius: "Lehrbuch der Elektrochemie," p. 186.

gives the volume containing a gram molecule of the salt; two, the percentage of hydrolysis; and column three, the hydrolysis constant as calculated by the equation previously used.

Table XIII.

$V.$	$100x.$	$10^{-5} \times K_{hydrolysis.}$	$V.$	$100x.$	$10^{-5} \times K_{hydrolysis.}$
32	0.46	15	64.0	0.66	15
(32)	(0.36)	(25)	95.6	0.75	17
32	0.43	17	95.6	0.82	12
64	0.72	12	191.3	1.27	12
64	0.61	17	382.6	2.00	10

Mean, 14×10^5

Mean by conductivity, 9.1×10^5.

The Velocity of Decomposition of the Hydrochlorides of Imidobenzoates.

In order to determine the reacting substance in the decomposition of an imidoester by water into an ester and ammonia (equation 2 or 2′), and to establish rigorously the cause of the acceleration of the decomposition by the addition of an acid, the velocity of the change of methyl imidobenzoate, in the presence of hydrochloric acid, was determined under varying conditions, at a temperature of 25° (+0°.01), and the experimental data subjected to analysis. In most of the experiments the hydrochloride of the imidoester was used alone; in other cases the experiments were carried out with an excess of the free base present with the hydrochloride. In either case, we have simultaneously two reactions taking place, with still a third reaction, according to equation (1), which is exceedingly slow and ordinarily negligible, but which was, nevertheless, taken into account, as previously described.[1] A condition of equilibrium is established between the salt, base, acid, and water according to equation (3), which is continuously disturbed by the water decomposing one of the constituents of the system into ammonium chloride and acid ester (equation 2′); the condition of equilibrium in (3) may be said to establish itself at each instant in conformity to the

[1] Stieglitz: *Loc. cit.*

changing conditions, since only direct, simple ionic reactions are involved; consequently, we have at every moment, according to Walker[1] and Arrhenius,[2] for the hydrolyzed salt solution, an equilibrium according to equation (3):

$$C_{salt} = K_{hydrolysis} \times C_{base} \times C_{acid}.$$

In the second place, the decomposition is proceeding with a measurable velocity, either the total substance, the salt and base indifferently, or only the free base or the salt (*i. e.*, its positive ions in the dilute solution used) reacting with water to give the products of the action represented in equation (2).[3]

The first possibility that the total substance, base and salt indifferently, enter into action with the water, may be taken to illustrate the principle of an acceleration produced by the acid present, an acceleration not due to the salt formation, which, of course, inevitably follows, but, in some mysterious way, to the mere presence of the acid in the system. For this case we have a monomolecular reaction proceeding with a velocity proportional to the total substance present.

$$\frac{dx}{dt} = k_{subst} \times C_{subst}. \qquad (5),^4$$

$$k_{subst} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (6).$$

The reliability of such an interpretation is best ascertained by applying the equation to the data obtained for velocity determinations, in which an excess of free base is added to the salt solution. The degree of hydrolysis, when the salt is used alone, being exceedingly small (see $100x$ in Tables IV., VI., etc.), the total substance is almost the same as the salt content. Column seven, Table XIV., gives the values for $k_{subst.}$ calculated under these conditions according to (6), and a comparison of experiment four, in which no excess of free base was present, with experiment five, where an ex-

[1] Z. physik. Chem., **4**, 319 (1889).
[2] *Ibid.*, **5**, 17, (1890).
[3] Stieglitz: *Loc. cit.*
[4] $C_{subst.}$ is a function of x.

cess of free base was used, shows that $k_{subst.}$ is no true constant.

The second possibility,

$$\frac{dx}{dt} = k_{base} \times C_{base}'$$

that the free base present in the hydrolyzed solution is the active substance present, represents another possibility of an enhanced reactivity, not due to salt formation simply, but to some other undiscovered property of the hydrochloric acid.[1] The analysis of this case is more complicated than the previous one. Stieglitz finds for this case that we would have

$$k_{base} = \frac{1}{K_v (t_2 - t_1)} \left[\sqrt{R - 4K_v x_1} - \sqrt{R - 4K_v x_2} + (1 - s - K_v) \log \text{nat} \frac{\sqrt{R - 4K_v x_2} + (1 - s - K_v)}{\sqrt{R - 4K_v x_1} + (1 - s - K_v)} \right] (7),$$

in which $R = (1 - s + k_v)^2 + 4K_v s$ and the total original concentration of the imidoester used, both as salt and as free base, is called one gram molecule in V liters, the known original concentration of the salt (the added acid) s gram molecules in V liters, and x_1 and x_2, the parts of a gram molecule in V liters decomposed in t_1 and t_2 minutes, respectively. For a given experiment V is a given number and K_v is used for $V / K_{hydrolysis}$, the latter being the hydrolysis constant of equation (3) as established by Tables IV., VI., etc. When no excess of free base is used ($s = 1$), the base present in the solution results entirely from the hydrolysis of the hydrochloride and we may calculate k_{base} from

$$k_{base} = \frac{2}{(t_2 - t_1)\sqrt{K_v}} \left[\sqrt{1 - x_1} - \sqrt{1 - x_2} \right] (8).^2$$

A few calculations of k_{base}, made according to (7) and (8), are given in column six, Table XIV., and comparison of the values of k_{base} in experiments three and five, in which excess of free base was absent and present, respectively, shows that k_{base} is as little a true constant as k_{subst}.

[1] See Stieglitz: Am. Chem. J., **39**, 402, in which such theories are critically considered.

[2] Stieglitz: *Loc. cit.*

In the third possibilty considered, the fact that addition of an acid accelerates the decomposition of an imidoester and at the same time forms its salt made it extremely probable, according to Stieglitz, that the reacting substance in equation (2) would be found to be rigorously the salt (the positive ions, in the dilute solutions used), in which case the reaction velocity would be accelerated simply in proportion to the increased concentration of the salt. For this case

$$\frac{dx}{dt} = k_{salt} \times C_{salt} \qquad (9)^1,$$

and we have:

$$k_{salt} = \frac{1}{t_2 - t_1}\left[\frac{1 - s + K_v}{1 - s} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} - (1 - s + K_v)}{\sqrt{R - 4K_v x_2} - (1 - s + K_v)} + \frac{1 - s - K_v}{1 - s} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} + (1 - s - K_v)}{\sqrt{R - 4K_v x_2} + (1 - s - K_v)}\right] (10),^2$$

or, considering only the values affecting the significant numbers in the result, we have the simpler expression:

$$k_{salt} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} - (1 - s + K_v)}{\sqrt{R - 4K_v x_2} - (1 - s + K_v)} \qquad (10'),$$

in which the symbols have the same significance as in (7). When $s = 1$, as is the case when no free base is added, we have

$$k_{salt} = \frac{1}{t_2 - t_1}\left[\log \text{nat} \frac{1 - x_1 - \sqrt{(1 - x_1)\frac{K_v}{}}}{1 - x_2 - \sqrt{(1 - x_2)\frac{K_v}{}}} - \sqrt{\frac{K_v}{1 - x_1}} + \sqrt{\frac{K_v}{1 - x_2}}\right] (11).$$

For less rigorous calculations, when $s = 1$, the salt being very little hydrolyzed, we may use the simple logarithmic form, for determining k_{salt}, with a sufficient degree of accuracy:

$$k_{salt} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (12).$$

The analysis of the experimental data as given in Table XIV., column five, shows that constant values for k_{salt} are obtained, regardless of the varying conditions used.

[1] C_{salt} is a function of x.

[2] Stieglitz: *Loc. cit.*

Ethyl Imidobenzoate.

The results obtained for ethyl imidobenzoate at 25° are given in Table XIV. In later tables the influences of added electrolytes (excess of acid) on the velocity of the reaction will be given, as well as the reaction velocities at lower temperatures than 25°.

In column one of the table are given the conditions of the experiment, the volume V containing one gram molecule of the total substance (free base and salt), s representing the proportion of salt used, and v the volume of solution taken for each titration. Column two gives the time in minutes; three, the cubic centimeters of tenth-normal alkali neutralized by the imidoester salt (see p. 439); four gives the percentage of substance decomposed in time t. In column five is given the constant for k_{salt} as calculated by means of equation (10), or, in the absence of an excess of free base, from (11) or (12). Column six shows the values of k_{base} as calculated by means of equation (7), while column seven gives the constant for k_{subst} as calculated with common logarithms according to equation (6).

Table XIV.—Ethyl Imidobenzoate at 25°.

	t.	v.	$100x$.	$10^5\ k_{salt}$.	k_{base}.	$43430\ k_{subst}$.
1.	0	11.99	5.03	...	....	....
$V = 20$	60	9.94	21.27	313	...	....
$s = 1$	120	8.26	34.58	312	....	....
	180	6.81	46.06	316	....	....
$v = 25$	620	1.64	87.00	323	....	....
		Mean: $k_{salt} = 0.00316$			....	....
2.	0	12.21	3.30	...	....	....
$V = 20$	60	10.14	19.69	310	....	....
$s = 1$	110	8.61	31.81	320	....	....
$v = 25$	300	4.85	61.59	310	....	....
		Mean: $k_{salt} = 0.00313$			...	....
3.	0	12.50	0.0	...	....	....
	5	12.18	2.56	...	....	....
$V = 20$	40	10.95	12.40	306	0.62	....
$s = 1$	80	9.71	22.32	304	0.60	....
$v = 25$	180	7.14	42.88	308	0.56	....
	300	4.96	60.32	306	0.51	..
	540	2.38	80.96	308	0.44	....
		Mean: $k_{salt} = 0.00306$				

Table XIV—(Continued).

	t.	v.	100 x.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
4.	(10)	(9.76)	(2.40)	...	....	...
	60	8.56	14.40	(262)	....	...
$V = 10$	120	7.11	28.90	310	....	134
$s = 1$	210	5.45	45.50	304	....	131
$v = 10$	270	4.55	54.50	304	....	131
	330	3.78	62.20	306	....	132
	450	2.62	73.80	306	....	132
	570	2.08	79.20	(276)	....	...

Mean: $k_{salt} = 0.00306$

5.	0	12.50	0.0	.	...	..
	10	12.18	2.56	..	....	..
$V = 20$	70	10.64	14.88	287	0.0084	98
$s = 0.75$	160	8.74	30.08	299	0.0074	96
$v = 25$	250	7.26	41.92	305	0.0063	94

Mean: $k_{salt} = 0.00297$

The grand average for k_{salt} is 0.00307.

Methyl Imidobenzoate.

The following table gives the data and the constants calculated for methyl imidobenzoate. As for the ethyl ester, K_{salt} is the only real constant under all conditions.

Table XV.—Methyl Imidobenzoate at 25°.

	t.	v.	100 x.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
1.	0	(10.05)	(20.4)	...	....	....
	60	8.76	30.62	...	....	....
$V = 20$	120	6.22	50.74	573	....	....
$s = 1$	180	4.44	64.83	568	....	....
$v = 25$	300	2.25	82.18	568	....	....

Mean: $k_{salt} = 0.00570$

2.	0	11.09	11.28	...	....	...
$V = 40$	40	8.51	31.92	...	....	...
$s = 1$	100	6.07	51.44	571	....	245
$v = 50$	170	4.06	67.52	577	....	247
	210	3.24	74.08	576	....	247
	270	2.31	81.52	576	....	246
	330	1.63	86.96	580	....	247
	390	1.16	90.72	580	....	248

Mean: $k_{salt} = 0.00577$

Table XV—(Continued).

	t.	v.	$100x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
3.	0	(12.50)	.....	...	....	....
	25	10.83	13.36	...	....	....
$V = 20$	65	8.67	30.64	560	....	....
$s = 1$	110	6.68	46.56	573	....	....
$v = 25$[1]	170	4.96	60.32	543	....	....
	260	3.18	74.56	530	....	....
	350	2.04	83.68	520	....	....
	440	1.18	90.56	541	....	....

Mean: $k_{salt} = 0.00545$

4.	0	(12.50)	....	...	....	...
	10	11.80	5.60	...	....	...
$V = 20$	40	9.89	20.88	(592)	0.771	(256)
$s = 1$	85	7.83	37.36	551	0.680	238
$v = 25$[2]	130	6.15	50.80	548	....	236
	220	3.83	69.36	541	0.560	233
	310	2.31	81.52	550	....	236
	400	1.42	88.64	550	0.430	235

Mean: $k_{salt} = 0.00548$

5.[3]	0	15.95	....	...	....	...
	5	15.38	3.57	...	....	...
$V = 15.7$	45	12.77	19.94	603	0.0195	202
$s = 0.784$	85	10.96	31.28	552	0.0165	184
$v = 25$	125	9.28	41.81	608	0.0151	183
	165	8.17	48.77	584	0.0129	172

Mean: $k_{salt} = 0.00587$

[1] $v = 50$ cc. for the seventh titration.

[2] $v = 50$ cc. for the sixth and seventh titrations.

[3] Taking into account the simultaneous very slow decomposition of the free base present into benzonitrile and methyl alcohol, according to the velocity constant as determined (see p. 86), we find for k_{salt} according to Stieglitz (*loc. cit.*):

t	45	85	125	165
$10^5 k_{salt}$	593	543	596	571

Mean: $k_{salt} = 0.00576$

Table XV—(Continued).

	t.	v.	$100\,x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
6[1].	0	12.50	...	...	....	...
	20	11.10	11.20	...	....	...
	60	9.35	25.20	540	0.0201	186
$V = 20$	115	7.49	40.08	568	0.0160	180
$s = 0.8$	205	5.40	56.08	568	....	170
$v = 25$	255	4.60	63.20	603	0.0707	162
	310	3.86	69.12	548	....	157

Mean: $k_{salt} = 0.00565$

Grand average: $k_{salt} = 0.00562$.

n-Propyl Imidobenzoate.

The next table gives the data for *n*-propyl imidobenzoate hydrochloride as determined and calculated for a temperature of 25°. The columns have the same significance as in the tables for the other esters.

Table XVI.—n-Propyl Imidobenzoate at 25°.

	t.	v.	$100\,x$.	$10^5 k_{salt}$.
	0	11.98	...	...
$V = 20$	20	11.21	5.73	297
	80	9.40	20.95	295
$s = 1$	140	7.89	33.64	294
	200	6.59	44.74	304
$v = 25$	260	5.59	52.99	292
	325	4.57	61.57	295
	380	3.88	67.37	290

Mean: $k_{salt} = 0.00295$

Methyl Metanitroimidobenzoate.

The next table gives the data for the decomposition velocity of methyl metanitroimidobenzoate and shows the constants obtained. Owing to the very rapid rate of change of this substance, accurate measurements at 25° were impossible and the experiments were therefore conducted at 18°.

[1] Allowing, as in (3), for the slow decomposition of the base, we have:

t	60	115	205	255
$10^5 k_{salt}$	540	558	571	580

Mean: $k_{salt} = 0.00562$

Table XVII.—Methyl Metanitroimidobenzoate at 18°.

	t.	v.	100 x.	$10^4 k_{salt}$.	k_{base}.	4343 $k_{subst.}$
1.	0	10.43	0.0	...	...	...
	11	7.91	24.14	256	...	109
	23	5.87	43.72	255	...	109
V = 20	35	4.33	58.47	257	...	109
s = 1	48	3.22	69.12	252	...	106
v = 25	63	2.28	78.14	249	...	105
	76	1.71	83.60	247	...	103
	88	1.27	87.82	248	...	104
	101	0.95	90.89	246	...	103
		Mean: k_{salt} = 0.0251				
2.	0	.....	.....	...	...	...
	6	10.71	13.02	...	...	...
V = 18.2	17	7.99	32.80	258	0.194	102
s = 0.909	28	6.04	46.98	255	...	98
v = 25	39	4.52	58.04	256	0.146	96
	51	3.31	66.84	257	...	93
	62	2.51	72.65	255	...	90
	73	1.85	77.45	259	0.104	87
		Mean: k_{salt} = 0.0257				
3.	0	10.78	0.0	...	...	...
V = 40	14	7.58	29.69	251	...	109
s = 1	27	5.54	48.61	254	...	107
v = 50	40	4.14	61.59	248	...	104
	52	2.95	72.64	258	...	108
	66	2.18	79.78	245	...	105
	78	1.66	80.61	(219)	...	104
	97	1.28	88.12	(230)	...	102
	103	0.95	90.10	(236)	...	103
		Mean: k_{salt} = 0.0251				

The Effect of an Excess of Hydrochloric Acid on the Velocity of Decomposition of the Imidobenzoate Esters.

The velocity of decomposition of the hydrochloride of methyl imidobenzoate into ammonium chloride and methyl benzoate was determined at 25° in the presence of excess of hydrochloric acid varying in amount from 0.05 to 0.5 mole, the salt solution being 0.05 molar. The experimental results are given below, and the conclusions based upon them follow the table. The velocity constant was calculated according to equation (12).

Table XVIII.—Methyl Imidobenzoate.

t.	*v.*	43430*k*.	*t.*	*v.*	43430*k*.
1. 0.05 salt, 0 acid.			2. 0.05 salt, 0 acid.		
0	11.80	....	0	10.83	...
30	9.89	(256)	40	8.68	240
75	7.83	237	85	6.68	(247)
120	6.15	236	145	4.96	234
210	3.83	233	235	3.18	227
300	2.31	236	325	2.04	(223)
390	1.42	235	415	1.18	232
	Mean,	235		Mean,	234
3. 0.05 salt, 0.05 acid.			4. 0.05 salt, 0.05 acid.		
0	12.19	...	0	10.79	...
40	9.78	239	40	8.88	(212)
80	7.81	241	85	6.82	235
120	6.26	241	120	5.64	236
220	3.81	230	185	4.00	233
	Mean,	238		Mean,	235
5. 0.05 salt, 0.10 acid.			6. 0.05 salt, 0.10 acid.		
0	12.00	...	0	(10.36)	...
40	9.95	(203)	40	8.82	...
80	8.00	220	120	5.73	234
120	6.28	234	180	4.21	229
160	5.25	224	260	2.97	215
240	3.56	220	340	1.81	229
320	2.48	214	420	1.16	232
	Mean,	222		Mean,	228
7. 0.05 salt, 0.15 acid.			8. 0.05 salt, 0.50 acid.		
0	11.53	...	0	11.15	...
35	9.50	(240)	40	9.35	191
75	8.18	199	80	7.86	190
115	6.70	205	120	6.47	197
155	5.33	216	160	5.55	189
235	3.70	210	240	3.88	191
315	2.24	226	300	3.01	190
395	1.56	220	360	2.47	182
	Mean,	213		Mean,	190
9. 0.05 salt, 0.50 acid.					
0	11.88	...			
35	10.27	181			
75	8.45	197			
115	6.98	201			
155	6.04	190			
195	4.97	194			
	Mean,	193			

Table XIX.—Ethyl Imidobenzoate.

t.	*v.*	$10^5 k_{salt}$.	*t.*	*v.*	$10^5 k_{salt}$.
1. 0.05 salt, 0 acid.			2. 0.10 salt, 0.10 acid.		
0	12.19	...	0	8.56	...
35	11.12	(262)	60	7.11	309
75	9.75	298	150	5.45	301
175	7.16	305	210	4.55	301
295	4.95	305	270	3.78	303
535	2.38	305	290	2.62	303
	Mean,	303		Mean,	303
3. 0.05 salt, 1 acid.			...	...	...
0	11.91	...	...	...	...
45	10.84	209	...	...	...
105	9.67	198	...	...	...
185	8.19	202	...	...	...
295	6.55	203	...	...	...
405	5.17	206	...	...	...
	Mean,	204			

According to the theory of Stieglitz,[1] the decomposition of imidoesters by water is caused by the action of the ions of water on the positive ions of the imidoester, according to

$$RC(:\overset{+}{N}H_2)OR + HOH \rightarrow RCO_2R + \overset{+}{N}H_4 \qquad (13).$$

Now, in the first place, an addition of an excess of hydrochloric acid must produce a depression of the degree of ionization of the imidoester salt, the salt ionizing in a mixture of electrolytes according to the concentration of the total electrolyte present. On the basis of the principle of isohydric solutions that solutions containing a positive or negative ion in common in the same concentration do not affect each other's ionization, one can imagine, with Arrhenius, for each of the above mixtures, the solvent so divided between the salt and the acid that solutions of like concentration of chlorine ions result, and the degree of ionization of the salt and acid in the resulting mixture may be calculated. For these calculations Schlesinger's[2] data on the degrees of ionization of the hydrochloride of methyl imidobenzoate were used, and allow-

[1] *Loc. cit.*

[2] See a later report by Schlesinger in Am. Chem. J.

ance was made for the greater degree of ionization of the hydrochloric acid, which results in the acid receiving a larger share of the water than would correspond to the molecular proportions. Table XX., page 469, gives in column one the excess of acid actually used and in column two the molecular concentration of the salt, *whose degree of ionization in pure aqueous solution would correspond to that of the salt in the mixture.* Column three gives the degree of ionization of the salt corresponding to these concentrations, and column four, the degree of ionization of the acid for the mixture. The interpolations necessary were made rectilinearly from the experimental values for the nearest molecular concentrations. It was not considered important to make more exact interpolations in this series, since the relations are being more rigorously investigated in this laboratory.[1] Column five shows the mean observed velocity constants, referred to the total salt, as obtained from Table XVIII., and column six gives the velocity constant referred only to the positive ion of the salt, k_{salt} being divided by α_{salt}.

In the second place, the addition of an excess of hydrochloric acid will have a so-called "salt-effect" on the decomposition of the imidoester salt by water,[2] as it has in other changes in which water acts, such as the catalysis of esters or of cane-sugars,[3] the "salt-effect" probably consisting, in this case, in an increase of the degree of the ionization of water, that is, it probably affects the concentrations of the reacting ions of water in the reaction expressed by equation (13). This "salt-effect" is most likely produced only by the ionized portion of the acids and salts, as suggested by Arrhenius, and as results obtained in this laboratory uniformly confirm. In the experiments under consideration, after allowing for the effect of the change of the degree of ionization of the imidoester salt, it will be noted (Table XX., column 6) that 43430 k/α rises from 275 for the 0.05 salt, without any excess of acid, to 400 for an excess of 0.5 mole of acid—that

[1] *Vide* a later article by E. E. Barnard.

[2] Stieglitz: Am. Chem. J., **39**, 166.

[3] Arrhenius: Z. physik. Chem., **1**, 126 (1887); **4**, 235 (1889). Euler: *Ibid.*, **36**, 419 (1901).

is, the accelerating salt effect of 0.5 mole of acid is $\frac{400-275}{275}$ or 46 per cent. As the degree of ionization of 0.5 normal hydrochloric acid is 84.3 per cent, the acceleration per gram equivalent of *ionized* acid is 109 per cent. It is a most striking fact that for the same excess of acid in the case of ethyl imidobenzoate, whose velocity constant is only half as great as that of the methyl ester, McCracken[1] found an accelerating effect of 107 per cent, and for ethyl metanitroimidobenzoate, the velocity constant of which is five times greater than the methyl ester constant, the observed accelerating effect was 110 per cent per gram equivalent of ionized acid. This remarkable agreement, thus showing these values to be independent of the velocity constants themselves, seems to confirm the view of this reaction adopted here[2] and justifies the following calculation of what the velocity constant should be[3] in each experiment given in Table XIX. We have:

$$K_{calc} = 262 \times \alpha_{salt} \times (1 + m_{salt} \times \alpha_{salt} + 1.09\, m_{acid} \times \alpha_{acid}) \quad (14).$$

In the equation, 262 represents the hypothetical velocity constant of decomposition of the methyl imidobenzoate in a solution of zero concentration, that is, completely ionized and free from any salt effect whatever, including the auto-salt effect as developed by Schlesinger.[4]

The factor α_{salt} in the above equation makes the velocity of decomposition proportionate only to the concentration of the positive ion of the imidoester salt. The expression in the brackets gives the acceleration due to the effect in the solution of water produced, first, by the ions of the salt and, secondly, by the ions of the hydrochloric acid. The acceleration produced by the salt itself, according to Schlesinger's results, as above mentioned, is just about 100 per cent per mole of ionized salt, and the effect of m_{salt} moles[5] of salt,

[1] *Vide* a later paper by McCracken in Am. Chem. J., and Stieglitz: Am. Chem. J., **39**, 166.

[2] Stieglitz: Am. Chem. J., **39**, 166.

[3] Stieglitz: *Loc. cit.*

[4] *Vide* a later article in Am. Chem. J. by H. I. Schlesinger.

[5] The real concentrations, m_{salt}, are found in Table XVIII. The values m'_{salt}, in Table XX, represent the ideal concentrations of an isohydric solution.

ionized to the extent of α_{salt} per cent, would be $m_{salt} \times \alpha_{salt}$. The average acceleration per 0.5 mole acid, dissociated to the extent of 84.3 per cent (in the mixed solutions), is 46 per cent, giving 1.09 as the acceleration per mole ionized acid. The acceleration due to m_{acid} mole of acid present is therefore $1.09 \times m_{acid} \times \alpha_{acid}$.

The last column in Table XX. gives the values of the velocity constant as calculated according to equation (14) and represents what the observed constants should be in each experiment if the velocity of the reaction in the equation (2′) is really a function only of the positive ion of the imidoester and of the ionization of water—the latter being considered dependent, in turn, on the total concentration of salt and acid ions present in the mixture. A comparison of the values in the last column with the actually observed constants (k_{obs}, column 5) shows, in fact, a most satisfactory agreement.

Table XX.

1	2	3	4	5	6	7
m_{acid}.	m'_{salt}.	$100\alpha_{salt}$.	$100\alpha_{acid}$.	$43430 \times k_{obs}$.	$\frac{43430\, k_{obs}}{\alpha_{salt}}$.	$43430 \times k_{calc}$.
0.0	0.0	100 0	....	...	(262)[1]	...
0.0	0.05	85.5	....	235	275	234
0.0	0.05	....	...	234	...	234
0.05	0.106	79.8	91.6	238	296	228
0.05	0.106	....	....	235	...	228
0.10	0.170	74.8	90.0	222	301	223
0.10	0.170	....	....	228	...	223
0.15	0.238	70.6	89.2	213	302	218
0.50	0.80	48.0	84.3	190	400	187
0.50	....	....	....	193	...	187

The Effect of Temperature on the Velocity Constants.

The velocity constants of the first four esters, except *n*-propyl, investigated were also determined at 18°, and in the cases of ethyl and methyl esters the reactions were followed at 0° as well. In the following table the columns and symbols have the same significance as in Table XIV. In all cases the hydrochlorides of the esters were used alone.

[1] Hypothetical, see Schlesinger: *Loc. cit.*

Table XXI.—Ethyl Imidobenzoate.

	t.	v_t.	100 x.	$10^5 k_{salt}$.
T = 18°	0	12.31	...	...
	50	11.46	6.89	143
	190	9.52	22.66	135
V = 20	280	8.42	31.59	136
s = 1	370	7.45	39.47	136
v = 25	462	6.62	46.21	135
	580	5.55	59.91	137
	1360	1.90	84.56	137
			Mean: k_{salt} = 0.00136	
T = 0°	0	12.44	...	....
	180	12.10	2.73	15.4
V = 20	480	11.57	6.99	15.1
s = 1	1230	10.43	16.17	14.3
v = 25	2670	8.43	32.24	14.6
	4210	6.82	45.17	14.3
	5620	5.46	56.11	14.7
			Mean: k_{salt} = 0.000147	

Summarizing the results given in Tables XIV. and XXI., we have as the effect of temperature on the velocity constant:[1]

T	0°	18°	25°
$10^5 k_{salt}$	15.4	136	307
Veloc. ratio	0.0502	0.433	1

Methyl Imidobenzoate.

	t.	v_t.	100 x.	$10^5 k_{salt}$
1.	0	11.08	...	...
T = 18°	45	9.99	9.82	(230)
V = 20	105	8.60	22.38	241
s = 1	195	6.82	38.44	249
v = 25	285	5.43	50.99	250
	375	4.35	60.74	249
	495	3.28	70.40	246
			Mean: k_{salt} = 0.00247	
2.	0	11.01	0.0	....
T = 0°	90	10.68	3.00	33.8
V = 20	390	9.70	11.90	32.5
s = 1	1165	7.92	28.06	28.3
v = 25	1705	6.88	37.50	27.4
	2605	5.21	52.68	28.8
	4045	3.61	67.21	27.4
			Mean: k_{salt} = 0.000297	

[1] The theoretical discussion of this effect is reserved for a later paper.—J. Stieglitz.

The effect of temperature change on the velocity constant is shown by the summary of Tables XV. and XXI.:

T	0°	18°	25°
$10^5\ k_{salt}$	29.7	247	562
Veloc. ratio	0.0529	0.440	1

Isopropyl Imidobenzoate.

	t.	v_t.	100 x.	$10^5 k_{salt}$.
1.	0	12.27	0.0	....
$T = 18°$	410	10.20	16.88	45.6
$V = 20$	1320	6.86	44.10	44.1
$s = 1$	1820	5.37	56.24	45.4
$v = 25$	2800	3.45	71.89	45.3
	3380	2.72	77.84	44.6
	4250	1.88	84.65	44.1

Mean: $k_{salt} = 0.000448$

The values of the velocity constants from Table XVII. and XXI. are:

T	18°	25°
$10^5 k_{salt}$	44.8	103
Velocity ratio	0.435	1

The Velocity of Reaction of the Free Imidoesters in Aqueous Solutions.[1]

Attention has been called to the fact that free imidoesters alone in water solution decompose very slowly, according to

$$RC(:NH)OR \rightarrow RCN + ROH \qquad (1),^2$$

and since this change is simultaneous with the main reaction of the ionized salt (the free base formed being due to hydrolytic dissociation), it was necessary to determine the velocity constant in order to correct the observed velocity constants and thus determine the true constant of the salt.[3] The two products of decomposition of the free esters are neutral substances, so that the course of the reaction could be followed

[1] See the detailed discussion of this reaction in Stieglitz's paper: Am. Chem. J., 39, 166.

[2] A nitrile is the main product. Probably a small amount of benzamide is also formed.

[3] A few calculations in which this correction has been applied are given in the footnote on page 28. It was found to be trifling.

simply by direct titration, from time to time, of measured volumes of solution with standard acid and methyl orange, taking, of course, the precautions regarding the end tint described under the analyses of the free esters. The reaction is a monomolecular one, proceeding according to

$$\frac{dx}{dt} = k_{ester} \times (C_{ester} - x),$$

and

$$k_{ester} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2}.$$

The following table shows the results obtained for the various esters at 18° and 25°. The columns and symbols have the same significance as in previous tables. Owing to the slight solubilities of these esters, dilute solutions were necessarily used:

Table XXII.—Ethyl Imidobenzoic Ester.

	t.	v_t.	100 x.	$10^5 k_{ester}$.
1.	0	3.65	...	...
$T = 18°$	1240	3.10	15.1	13.2
$V = 60$	2140	2.74	24.9	13.4
$v = 25$	3560	2.25	38.4	13.6
			Mean: k_{ester} =	0.000134
2.	0	6.19	0.	...
	350	5.63	9.10	27.1
$T = 25°$	1110	4.57	26.2	27.3
$V = 40$	1580	4.01	35.2	27.5
$v = 25$	2480	3.04	50.9	28.7
	3220	2.43	60.7	29.0
	3940	1.98	68.0	28.9
	5380	1.38	77.7	27.9
	6800	0.96	84.5	27.4
			Mean: k_{ester} =	0.0002797

Methyl Imidobenzoic Ester.

1.	0	3.23	0.	...
	1790	2.57	20.4	12.8
$T = 18°$	2720	2.25	30.3	13.3
$V = 31$	4120	1.91	40.9	12.8
$v = 10$	5560	1.56	51.7	13.4
	7000	1.34	58.5	12.6
			Mean: k_{ester} =	0.000130

Table XXII—(Continued).

	t.	v_t.	100 x.	$10^5 k_{ester}$.
2.	0	12.49	0.0	...
T = 25°	200	11.85	5.05	25.9
V = 20	400	11.28	9.62	25.3
v = 25	1340	8.66	30.6	27.3
	2750	5.72	54.2	28.4
	4200	3.75	70.0	28.6
			Mean: k_{ester} = 0.000271	

Isopropyl Imidobenzoic Ester.

1.	0	1.513	0.0	...
T = 18°	2340	1.319	12.8	5.85
V = 150	3750	1.247	17.7	5.16
v = 25	5180	1.141	24.6	5.45
	6600	1.054	30.3	5.48
	8070	0.962	36.4	5.61
	13890	0.696	54.0	5.59
			Mean: k_{ester} = 0.0000552	
2.	0	2.012	0.0	...
	490	1.938	(3.66)	(7.6)
T = 25°	1230	1.702	15.42	13.6
V = 125	1790	1.600	20.5	12.8
v = 25	2670	1.438	28.5	9.9
	4100	1.180	41.3	13.0
	5560	0.962	52.3	13.3
	7020	0.818	59.3	12.8
			Mean: k_{ester} = 0.000126	

Methyl Metanitroimidobenzoic Ester.

1.	0	2.40	0.0	...
T = 18°	420	2.27	7.58	(18.70)
V = 208	1400	2.17	9.58	9.19
v = 50	2730	1.95	18.76	7.69
	4170	1.74	27.5	7.71
			Mean: k_{ester} = 0.000075	

It is evident that, in every instance, good constants are obtained for a reaction proceeding with a velocity proportionate to the total concentration of the ester.

It is with pleasure that I acknowledge the painstaking care with which Professor Stieglitz directed and followed my work, and I wish to express to him my appreciation and deep gratitude for all he has helped me to accomplish.